Some Aspects of Neutron Single Crystal Analysis[*]

Ray Pepinsky
Department of Physics,
The Pennsylvania State College

Introduction

This paper presents a few observations on single-crystal analysis, based upon experience with the method at the Brookhaven National Laboratory reactor during part of the summer of 1952, and a comparison of neutron and X-ray scattering.

The writer is deeply indebted to Dr. Andrew McReynold and his group at the Brookhaven National Laboratory for furnishing the complete facilities with which the KH_2PO_4 analysis was possible, and continual aid during the investigation. Discussions with Drs. McReynold, L. Corliss, J. Hastings and R. Weiss were extremely helpful, as was correspondence with Drs. H. Levy and S. W. Peterson of the Oak Ridge National Laboratory.

Fourier Methods in Neutron Analysis

One previous writer[1,2] has held that Fourier methods will not be possible for crystal analysis from neutron scattering data because of

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the nature of the nuclear form factors. Thewlis[3] has suggested that the application of a strong artificial temperature correction could overcome this difficulty. Other convergence factors could also be used[4,5], however, to provide better approximations to the correct density distributions. But it should be noted that this non-convergence is a problem only for simple structures in which most atoms are in special positions. In such cases Fourier methods are likely to be unnecessary anyway. As indicated by Wilson and co-workers[6], the Fourier coefficients for random structures comprised of point atoms, none of which possess excessively large scattering power, fall off with increasing scattering angle, in a manner depending upon the crystal symmetry. When the effect of thermal oscillations are superposed on this convergence, it can be expected that little additional convergence factor will be required for complex structures.

This conclusion has been born out very well in the case of the $(h,k,0)$ projection of KH_2PO_4, single-crystal neutron scattering data for which was recently collected by B. C. Frazer and the writer at the Brookhaven National Laboratory reactor. The structure, and particularly the $(0,0,1)$ projection, is actually not a favorable one from the point of view of the Wilson statistics. Phosphorus and potassium atoms are in special positions on the 4-fold axes, and are superposed in the $(0,0,1)$ projection. Nonetheless, the observed structure factors fall off sufficiently fast with increasing $\frac{\sin \theta}{\lambda}$ to permit computations of excellent Patterson and Fourier maps. The Patterson map showed well-defined negative peaks representing the vectors between negatively-scattering hydrogen and positively-scattering

P, K and O nuclei, and well-defined positive peaks for the other interatomic vectors. Approximate hydrogen positions could be assigned, then, directly from the Patterson map. The Fourier map for the nuclear density distribution shows the P, K and O nuclei, and the protons appear in double minima between the O-H...O bonded oxygens, with apparently half a proton, on the average, occupying each of the doubled positions. Patterson and nuclear density maps were also computed using calculated coefficients, assuming a single H-minimum between O-H...O oxygens, and with temperature-corrected scattering factors for the P, K and O atoms as deduced from the X-ray analysis of KH_2PO_4 and a temperature correction for the H-atoms as found by Levy and Peterson in NH_4Cl[8] These were in good agreement with the maps utilizing observed data, except for the appearance in the latter maps of the doubled (disordered) hydrogen positions.

The statistical convergence of neutron scattering factors in more or less random structures, coupled with the effects of natural thermal oscillation or artificial convergence factors, thus will evidently permit the rather general use of Fourier methods in neutron crystallography. This permits a much more optimistic view of the power of the neutron technique than has been presented heretofore.

Examples of Negligible Influence of Extinction

It has also been held that the effects of extinction may very seriously limit the size of crystals which can be used in single crystal analyses[9,10]. In the case of the KH_2PO_4 study reported above, a cylindrically-ground c-axis crystal about 3 mm. in diameter and 1 cm. long was

utilized. The crystal was dipped several times into liquid nitrogen, in order to carry it back and forth through the ferroelectric transition point from tetragonal to orthorhombic symmetry. Extinction effects were found to be negligible. It is questionable whether the low-temperature treatment was necessary, but it was employed because of the limited time available, which time would not have sufficed to permit repetition of the measurements. The smallness of the influence of extinction has been reported previously by Levy and Peterson, in the case of NH_4Cl single crystals[8].

Phase Determination from Neutron Data

It is well known that the chief difficulty in X-ray structure analysis is the absence of direct information on the phases of the scattered X-rays. Methods have been introduced, based upon non-negativity and "atom-icity" of the electron distribution, which do permit deduction of some phase information[11,12]. "Marked atom" methods (heavy atoms, with or without iso-morphous replacement) have been particularly advantageous[13].

In their first paper on algebraic relations, Harker and Kasper[14] pointed out that their phase-determining conditions were strengthened if the observed crystal structure factors were divided by the value for the same scattering angle of the atomic structure factor for an "average" type of atom in the structure, the "average-atom" factor being corrected for temper-ature oscillation. The effect of this modification of the observed structure-factor amplitudes is to simulate Fourier coefficients for a point-atom structure without thermal vibrations; and such point-atom coefficients afford the strongest phase-determining conditions. It is unfortunately true that in

the majority of structures involving different kinds of atoms, the structure-factors for these atoms are not sufficiently similar in form to permit choice of an "average" atom which will lead to accurate coefficients for the point-atom structure; and thus there is introduced into the already complex phase-determination algebra the further complication of inexact data.

It is interesting to note that neutron scattering factors are just those corresponding to thermally-oscillating point atoms; and thus the only correction needed to reduce the Fourier coefficients to those for a distribution of fixed point-scatterers is to correct for the temperature effects. This can generally be done with much greater accuracy than is possible in the correction for atomic structure factors, and it must be done in both cases (for either nuclear scatterers or electron cloud distributions). Therefore, neutron scattering data is more amenable to algebraic phase-determining methods than is X-ray data.

Marked Atom Methods

The effects on structure analysis of variation of neutron scattering power for the various nuclei in the periodic table have been discussed in several other places. A few such effects should be particularly noted here. In one sense the "heavy-atom" method of X-ray analysis is possible to a very much more limited extent with neutrons, since the variation of scattering cross-sections is random throughout the periodic table, and the coherent scattering cross-sections do not vary much from one element to another. Striking use of the isomorphous replacement method is possible with replacement of hydrogen by deuterium. The coherent scattering cross-section here changes

from -0.38 for H to +0.64 for D. The incoherent scattering of H may be troublesome in some cases, although to a very much lesser extent with single crystals than in powder diffraction — as Levy and Peterson[8] and others have pointed out. The small influence of H-atoms upon X-ray scattering is of course an advantage in many-atom organic structures, where location of non-hydrogen atoms is already difficult and the structures would probably be impossible to determine if many hydrogen parameters would also have to be established before structure factors could be calculated. In structures where hydrogen positions are important, the obvious procedure is to determine non-H atom coordinates with X-rays, and then locate H (or D) atoms with neutrons.

Isomorphous replacement depends of course upon both chemical and packing-size similarities in the replaceable atoms. If enriched isotopes were readily available, isotopic replacement would be very advantageous in the cases (including H) shown in Table I. Data for this table and the discussion below are from C. Shull and E. O. Wollan, of the Oak Ridge National Laboratory[15].

Whereas replacement of halogens is very useful in the X-ray iso-morphous methods, Cl is the only outstandingly heavy scatterer among these for neutrons. S (0.31) and Se (0.89) are good pairs for neutron studies. Na or K (0.35), Rb (0.55), Cs (0.49) and Tl (0.75) are not as advantageously different as in the X-ray case; but replacement of NH_4 by K, Rb, or Tl should provide interesting and perhaps useful effects. Ca, Sr and Ba are not suf-ficently different to be useful in the neutron case. Ti (-0.38) and Zr (+0.62) are an extremely good pair for the isomorphous replacement method.

Table I.

Isotopes for Use in Isomorphous Replacement Method

Isotope	Scattering factor $\times 10^{-12}$ cm.
^{1}H	-0.38
^{2}H = D	+0.65
^{6}Li	0.7
^{7}Li	-0.25
Li*	-0.18
Ca*	0.49
^{44}Ca	0.18
^{54}Fe	0.42
^{56}Fe	1.01
^{57}Fe	0.23
Fe*	0.96
^{58}Ni	1.44
^{60}Ni	0.30
^{62}Ni	0.87
Ni*	1.03
^{107}Ag	0.83
^{109}Ag	0.43
Ag*	0.61

* in natural abundance ratio

Scattering with negative phase occurs for H, ^{7}Li and Li in natural abundance ratio, Ti, Mn, and ^{62}Ni. As in the case of the KH_2PO_4 Patterson map, vectors between positive and negative scattering centers will appear in the Pattersons as negative peaks; all other interactions produce positive peaks. The aid which this provides in identification of the atoms responsible for the peaks is obvious.

It must of course be borne in mind that the algebraic relations in X-ray analysis which depend upon non-negativity of the distribution of scattering material will not apply without modification when negative scattering centers are present in the neutron case. Boundedness of the function can however be utilized[16]; and when the position of negative scatterers is known but the distribution of other nuclei is not yet established, a set of Fourier coefficients for the negative scatterers alone can be computed, and these can be subtracted from the corresponding coefficients for the complete crystal. Relations arising from non-negativity can then be applied.

Conclusions

Neutron diffraction has been regarded by some workers as a supplement to X-ray methods, to be used chiefly for structure refinement or location of light X-ray scatterers among heavy scatterers. There are cases, however, where neutron methods should provide more direct approaches to an unknown structure from the outset. Although it has been stated that Fourier methods will not be possible with neutron data, it is demonstrated both experimentally and theoretically that this is not true in cases where such methods will really be advantageous — i.e., for structures where the atoms are for the most part not in special positions.

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